

Quality Assessment Report for Water Quality Monitoring

April - June 2005



**Submitted to the
Technical Oversight Committee**

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Quality Assessment Report for Water Quality Monitoring April – June 2005

I. Introduction

This report is an assessment of the District laboratory analysis and field sampling for Total Phosphorus (TP) monitoring primarily for the following projects/stations during the 2nd quarter of 2005:

- Conservation Area Inflow and Outflows (CAMB)
S12A, S12B, S12C S12D, S333
- Everglades National Park Inflow Monitoring (ENP)
S175, S176, S177, S18C, S332, S332D
- Everglades Protection Area (EVPA)
LOX3 to LOX16
- Non-Everglades Construction Project (NECP)
S334

Since field QCs are collected for trips that include multiple project samples for the stations of interest, the report may also cover information on stations or project other than those listed above.

The District's Field Sampling Quality Manual states the minimum requirement followed in field sample collection. The Laboratory Quality Manual states the minimum requirement followed in laboratory sample preparation and analysis, as well as in data verification and validation. The results of laboratory and field quality control during this quarter are presented in Sections II and III of this report.

II. Field Sampling Quality Assessment

A. Quality Control

Field QC measures consist of equipment blanks (EB), field cleaned equipment blanks (FCEB), field blanks (FB), split samples (SS) and replicate samples (RS). Table 1 summarizes EB and FCEB results for all projects of interest to the TOC. All of 185 blanks were within the acceptance criteria. Table 2 summarizes field precision results. Field sampling precision was acceptable.

Data not meeting the set criteria for blanks, field precision or sampling protocols are flagged using FDEP data qualifier codes. A comprehensive list of flagged data for all trips that include samples for CAMB, ENP, EVPA and NECP during this quarter is presented in Table 3.

B. EVPA-Refuge LOX stations Sampling

A thorough assessment of the quality of May and June 2005 sampling events were documented in a report titled Assessment of the Quality of May-June 2005 TP Data and the Monitoring Processes for EVPA (LOX) Project (D. Ivanoff, Version 9/08/05 Report to SFWMD Management). The overall assessment indicates problems with the quality of collection and the resulting data. All data for all samples collected during these two sampling events were qualified. Long-term corrective action plans were also identified, to help to minimize the possibility of recurrence of identified problems. Re-training of field sampling staff, discussion of sampling procedures, and finalizing the monitoring plan were among the immediate corrective action identified.

Table 1. Field and equipment blank results

Type of Blank	Project	# Blanks collected	% ≤ 0.002
EB	CAMB	48	100
	ENP	3	100
	EVPA	2	100
	NECP	1	100
FCEB	CAMB	76	100
	ENP	23	100
	EVPA	13	100
	NECP	6	100
FB	CAMB	6	100
	ENP	2	100
	EVPA	5	100

**Note: There were also incidences of six (6) high values for field-cleaned equipment blanks associated with the May and June 2005 LOXA (expanded WCA1) sampling trips conducted by the same sampling team. The high equipment Blanks were for TP, Alkaline Phosphatase Activity, Orthophosphate, NO_x, Ammonia, Silica, Total Dissolved P, and Sodium. The blank value for TP was 0.061 mg/L; it was re-analyzed by the District laboratory for confirmation (0.060 mg/L). The high blank values may really be an indication of contamination or a result of sample mix-up, but in either case, is an indication of sampling error. All samples associated with this trip were flagged with a "V" qualifier.*

Table 2. Field precision summary

Project Code	Numbers of triplicates	Mean % RSD	Comments
CAMB	3	10.5	Precision criteria were met
ENP	1	2.8	Precision criteria were met
EVPA	3	5.2	Precision criteria were met
NECP	3	1.6	Precision criteria were met

Notes

- 1) Collection was done by either the District staff or its contractors (Refuge, ENP, DERM, Broward County DPEP, or private). Project management and collection for LOXA is handled by the Refuge.
- 2) All TP analyses were conducted by the District's Chemistry laboratory.
- 3) Field precision acceptance criteria: <20%. This criteria was applied only if sample values >PQL.
- 4) FB, FCEB and EB acceptance criteria: Must be \leq MDL.
- 5) Associated samples are flagged when concentrations are less than five times the resulting blank values for possibility of contamination.

Table 3. List of TP flagged data

PROJECT	SAMPLE ID	STATION ID	DATE COLLECTED	SAMPLE TYPE	TP, mg/L
EVPA	P22546-10	LOX7	5/2/2005	SAMP	0.108
EVPA	P22546-11	LOX4	5/2/2005	SAMP	0.043
EVPA	P22546-12	LOX4	5/2/2005	FCEB	<0.002
EVPA	P22546-2	S5AD	5/2/2005	SAMP	0.204
EVPA	P22546-3	S5AD	5/2/2005	RS	0.201
EVPA	P22546-9	LOX8	5/2/2005	SAMP	0.046
EVPA	P22547-10	LOX12	5/3/2005	SAMP	0.009
EVPA	P22547-11	LOX12	5/3/2005	FCEB	<0.002
EVPA	P22547-2	LOX6	5/3/2005	SAMP	0.049
EVPA	P22547-5	LOX11	5/3/2005	SAMP	0.069
EVPA	P22547-6	LOX13	5/3/2005	SAMP	0.015
EVPA	P22547-7	LOX14	5/3/2005	SAMP	0.018
EVPA	P22547-8	LOX16	5/3/2005	SAMP	0.012
EVPA	P22547-9	LOX15	5/3/2005	SAMP	0.009
EVPA	P22548-1	S5AD	6/13/2005	EB	<0.002
EVPA	P22548-10	LOX7	6/13/2005	SAMP	0.022
EVPA	P22548-11	LOX4	6/13/2005	SAMP	0.016
EVPA	P22548-12	LOX4	6/13/2005	FCEB	<0.002
EVPA	P22548-2	S5AD	6/13/2005	SAMP	0.145
EVPA	P22548-3	S5AD	6/13/2005	RS	0.149
EVPA	P22548-4	S5AD	6/13/2005	RS	0.151
EVPA	P22548-5	LOX3	6/13/2005	SAMP	0.023
EVPA	P22548-6	LOX5	6/13/2005	SAMP	0.026
EVPA	P22548-7	LOX10	6/13/2005	SAMP	0.027
EVPA	P22548-8	LOX9	6/13/2005	SAMP	0.027
EVPA	P22548-9	LOX8	6/13/2005	SAMP	0.018
EVPA	P22549-10	LOX12	6/14/2005	SAMP	0.007
EVPA	P22549-11	LOX12	6/14/2005	FCEB	<0.002
EVPA	P22549-2	LOX6	6/14/2005	SAMP	0.014
EVPA	P22549-5	LOX11	6/14/2005	SAMP	0.037
EVPA	P22549-6	LOX13	6/14/2005	SAMP	0.011
EVPA	P22549-7	LOX14	6/14/2005	SAMP	0.014
EVPA	P22549-8	LOX16	6/14/2005	SAMP	0.038
EVPA	P22549-9	LOX15	6/14/2005	SAMP	0.007

Notes: (1) All data in Table 3 were flagged with a "?"; sampling quality is questionable based on sampling assessment findings. The following analytes for the May and June 2005 sampling events for the LOX 3-16 were also flagged for the same reason: Alkaline Phosphatase Activity, Alkalinity, Ammonia, Calcium, Dissolved and Total Organic Carbon, Chloride, Color, Dissolved Oxygen, Hardness, Total Iron, Dissolved Kjeldahl Nitrogen, Total Kjeldahl Nitrogen, Magnesium, Nitrate+Nitrite, Nitrate, Nitrite, pH, Total Dissolved Phosphate, Orthophosphate, Potassium, Silica, Sodium, Specific Conductivity, Sulfate, Total Dissolved Solids, Total Suspended Solids, and Turbidity.

(2) Aside from TP data, data for six (6) LOXA (May and June sampling events) Equipment Blanks were also flagged for Alkaline Phosphatase Activity, Orthophosphate, NO_x, Ammonia, Silica, TP, Total Dissolved P, and Sodium.

Table 4. Samples not collected (Missing TPO4 results) or rejected by laboratory

Project	Date Collected	Station	Comments
CAMB	18-Apr-05	S12A	No flow, no samples collected
CAMB	16-May-05	S12A	No flow, no samples collected
CAMB	31-May-05	S12A	No flow, no samples collected
CAMB	13-Jun-05	S12A	No flow, no samples collected
CAMB	4-Apr-05	S12B	No flow, no samples collected
CAMB	2-May-05	S12B	No flow, no samples collected
CAMB	31-May-05	S12B	No flow, no samples collected
CAMB	13-Jun-05	S12B	No flow, no samples collected
CAMB	5-Apr-05	S12C	No flow, no samples collected
CAMB	2-May-05	S12C	No flow, no samples collected
CAMB	31-May-05	S12C	No flow, no samples collected
CAMB	2-May-05	S12D	No flow, no samples collected
CAMB	27-Jun-05	S333	No flow, no samples collected
ENP	5-Apr-05	S18C	No flow, no samples collected
ENP	12-Apr-05	S18C	No flow, no samples collected
ENP	19-Apr-05	S18C	No flow, no samples collected
ENP	20-Apr-05	S18C	No flow, no samples collected
ENP	26-Apr-05	S18C	No flow, no samples collected
ENP	3-May-05	S18C	No flow, no samples collected
ENP	10-May-05	S18C	No flow, no samples collected
ENP	17-May-05	S18C	No flow, no samples collected
ENP	24-May-05	S18C	No flow, no samples collected
ENP	28-Jun-05	S176	No flow, no samples collected
ENP	13-Apr-05	S332D	No flow, no samples collected
ENP	31-May-05	S332D	Sample not acidified (improper preservation); rejected by the lab
EVPA	4-Apr-05	LOX3	Tdepth<0.10 m, no samples collected
EVPA	2-May-05	LOX3	Tdepth<0.10 m, no samples collected
EVPA	4-Apr-05	LOX5	Tdepth<0.10 m, no samples collected
EVPA	2-May-05	LOX5	Tdepth<0.10 m, no samples collected
EVPA	4-Apr-05	LOX9	Tdepth<0.10 m, no samples collected
EVPA	2-May-05	LOX9	Tdepth<0.10 m, no samples collected
EVPA	2-May-05	LOX10	Tdepth<0.10 m, no samples collected
NECP	27-Jun-05	S334	Gate closed, no flow, no sample collected

III. Laboratory Quality Control Assessment

Routine laboratory QC samples include method blanks, detection limit checks, QC checks, matrix spikes, and precision checks. The laboratory's protocols include evaluation of initial calibration prior to analysis of samples and running continuing calibration verification checks, QCs, and continuing calibration blanks (CCBs). For laboratory method blanks, i.e. analyte-free water that are processed and analyzed in the same manner as regular samples, the laboratory's protocols require that no analysis proceeds when method blank exceed current MDL, which is 0.002. The analyst is required to troubleshoot and recalibrate if method blanks exceed this criteria. During this quarter, the both the mean and maximum blank result were <0.002 mg/L.

Figures 1-6 show recoveries from various levels of QC samples for the TP analysis at SFWMD laboratory. Statistical evaluation of precision and matrix spikes recoveries is also included. A portion of or an entire analytical run is generally rejected if QC recoveries are outside the set limits. Data is flagged accordingly if any deficiency is noted and the samples have exceeded the required holding times and can not be reanalyzed.

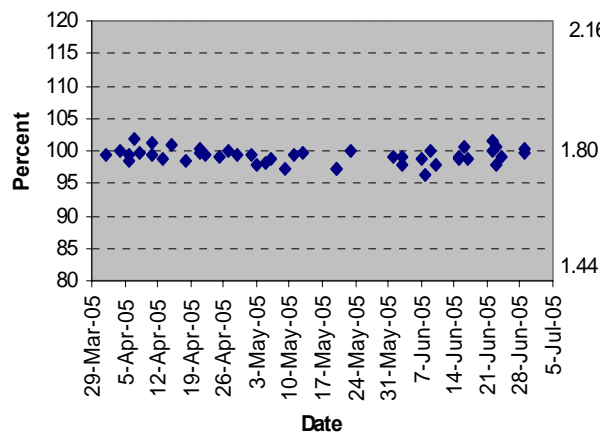
Recoveries for the QC samples are generally within $\pm 10\%$ from the true value, which are acceptable. The MDL check (QC5), with a true value of 0.004 mg/L, had a mean recovery of 100.0%. The MDL check daily results indicate the laboratory consistently achieved the 0.002 mg/L MDL.

An organic check is a solution prepared from phytic acid, a stable form of organic phosphate. Recoveries for this check sample are between 96.4 – 101.7%, indicating that the digestion process was effective. The same material is used to prepare matrix spikes, the mean recovery for which was 100.2%. One spike result, i.e. L27202-17, an estuarine sample from St. Lucie Estuary, and unrelated to the projects covered by the Settlement Agreement, had a recovery of 58.6%; the sample was flagged due to matrix interference.

The precision target for TP analysis during this period was 10.0%; mean %RPD achieved was 1.9% and 1.2% for low (0 to 0.200 mg/L) and high level (0.200-2.00 mg/L) analyses, respectively. The maximum RPD during this period were 7.2% and 3.9% for low and high levels, respectively.

Fig. 1

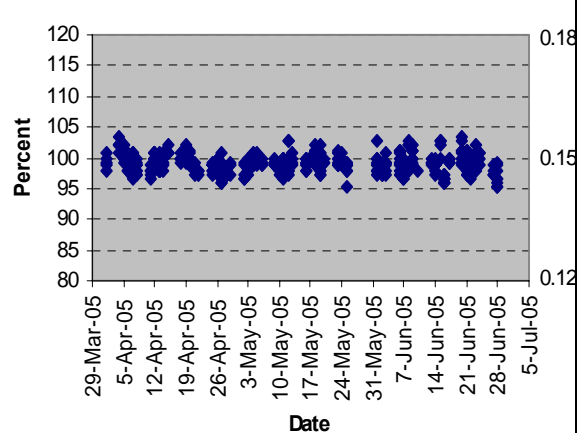
TP Organic Check Recovery
(TV=1.80 mg/L)



Mean = 99.2%, Max = 101.7%, Min = 96.4%

Fig. 2

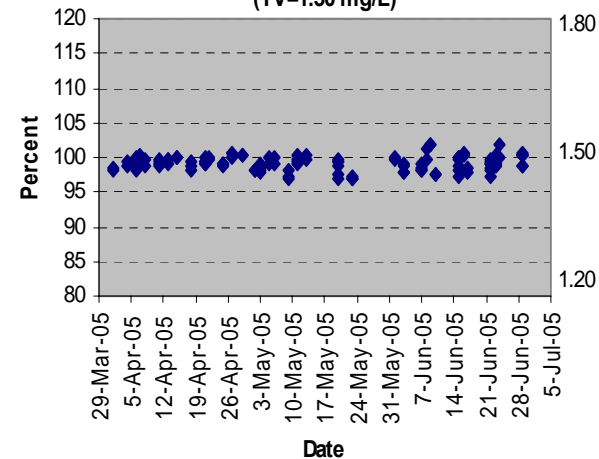
TP QC1 Recovery
(TV=0.150 mg/L)



Mean = 99.2%, Max = 103.3%, Min = 95.3%

Fig. 3

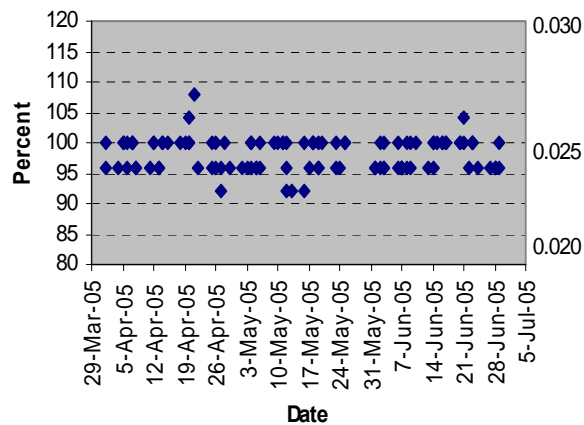
TP QC2 Recovery
(TV=1.50 mg/L)



Mean = 99.2%, Max = 101.9%, Min = 96.9%

Fig. 4

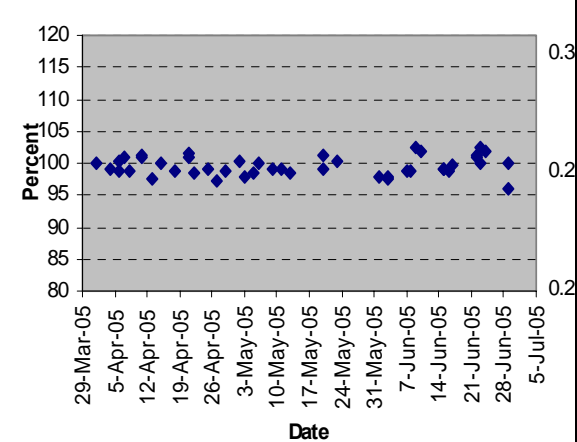
TP QC3 Recovery
(TV=0.025 mg/L)



Mean = 98.1%, Max = 108%, Min = 92.0%

Fig. 5

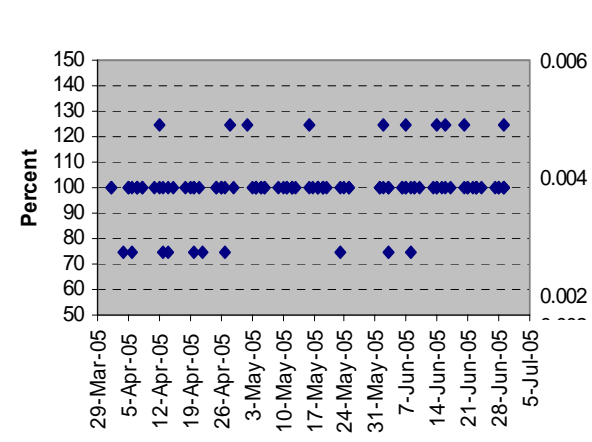
TP QC4 Recovery
(TV=0.250 mg/L)



Mean=99.6%, Max=102.4%, Min=96%

Fig. 6

TP MDL Check Recovery
(TV=0.004 mg/L)



Mean = 100.0%, Max = 125.0%, Min = 75.0%

<p>Laboratory Method Blanks Acceptance Limit = <0.002</p> <p>Max = 0.001 Mean = <0.002 Std. Dev = 0.0005 UCL = 0.002</p>	<p>TP Spike Recovery Data 4/1/05-6/30/05 Acceptance Limit = 90-110%</p> <p>Min = 58.6* Max = 110% Mean = 100.2% Std Dev = 4.32 3xSD = 12.95 LCL = 87.2% UCL = 113% n=335</p>
<p>TP Precision Data, Low Level (0-0.200) 4/1/05-6/30/05 Acceptance Limit = <10%</p> <p>Max = 7.2 Mean = 1.9 Std Dev = 1.61 3xSD = 4.83 UCL = 6.7 n = 277</p>	<p>TP Precision Data, High Level (0.20-2.00) 4/1/05-6/30/05 Acceptance Limit = <10%</p> <p>Max = 3.9 Mean = 1.2 Std Dev = 0.87 3xSD = 2.60 UCL = 3.8 n = 42</p>

IV. Inter-Laboratory Quality Control Assessment

A. Split Studies Between SFWMD and FDEP Laboratories

To continually assess comparability of results, the District sends split samples to other laboratories on a routine basis. Data from split studies between DEP and SFWMD laboratories from March 2004 to March 2005 for the following programs were used in this analysis: EVPA Quarterly Splits (EVPA), Everglades TP Round Robin (ERR), and S332 sites (C111).

The summary statistics and signed rank test for SFWMD vs. DEP results, as presented in Table 5, shows that the p-value for TP >0.020 mg/L and TP <0.020 mg/L levels are 0.0071 (Signed rank sum) and 0.0468 (t-test), respectively. However, the mean and median of differences from both laboratories are <0.004. These differences are around the laboratories' MDLs, which are 0.002 and 0.004 mg/L for SFWMD and DEP laboratories, respectively. At these levels, wider variability can be expected, even within each laboratory.

Table 5. Summary Statistics for Split Samples Between SFWMD and FDEP Laboratories

Summary Statistics for TP <0.02 mg/L				
Lab	N	Mean	Median	
FDEP	13	0.015	0.017	
SFWMD	13	0.012	0.011	
Statistical Test of Hypotheses				
Summary Of Paired Differences		Hypothesis	Statistical Test	Pvalue
Mean Of Differences	-0.003	Mean of Differences = 0	Student's t	0.0468
Median Of Differences	-0.002	Median of Differences = 0	Signed Rank	0.0225
Summary Statistics for TP >=0.02 mg/L				
Lab	N	Mean	Median	
FDEP	27	0.114	0.050	
SFWMD	27	0.111	0.047	
Statistical Test of Hypotheses				
Summary Of Paired Differences		Hypothesis	Statistical Test	Pvalue
Mean Of Differences	-0.004	Mean of Differences = 0	Student's t	0.0261
Median Of Differences	-0.002	Median of Differences = 0	Signed Rank	0.0071

Regression analysis of the data set was done separately for TP > 0.020 mg/L and for TP < 0.020 mg/L. Logarithmic transformation was done for TP > 0.020 mg/L, due to skewed data distribution. Logarithmic transformation was not needed for TP < 0.020 mg/L due the fact that distribution at that concentration range is approximately normal. Regression analyses for both < 0.020 and > 0.020 mg/L indicate that the slope is not significantly different from 1 and intercept is not significantly different from 0, indicating that the data from the two laboratories are highly comparable (Figures 7 and 8).

These statistical analyses and findings were consistent with what was in FDEP Data Comparability Report (Nearhoof, presentation to TOC, 8/26/04).

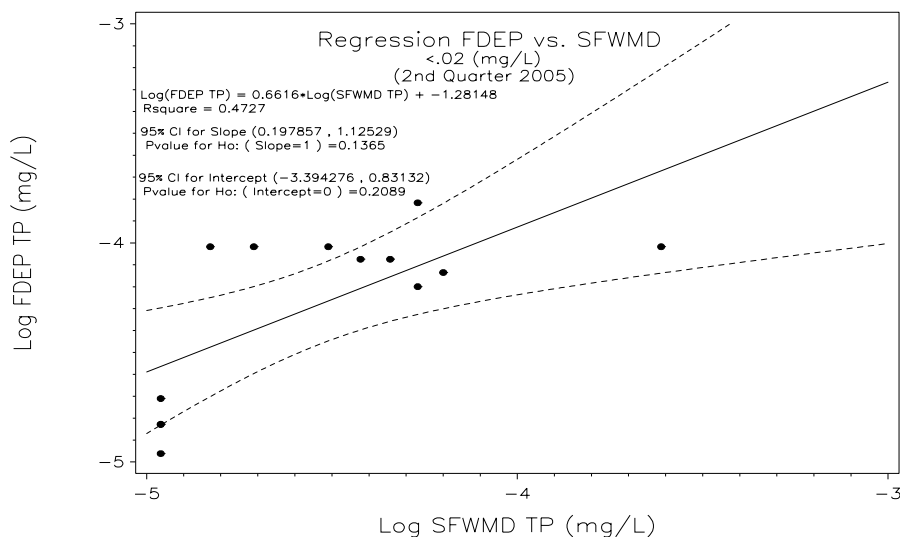


Figure 7. Regression analysis of TP (<0.02 mg/L) recoveries from SFWMD vs. DEP laboratory

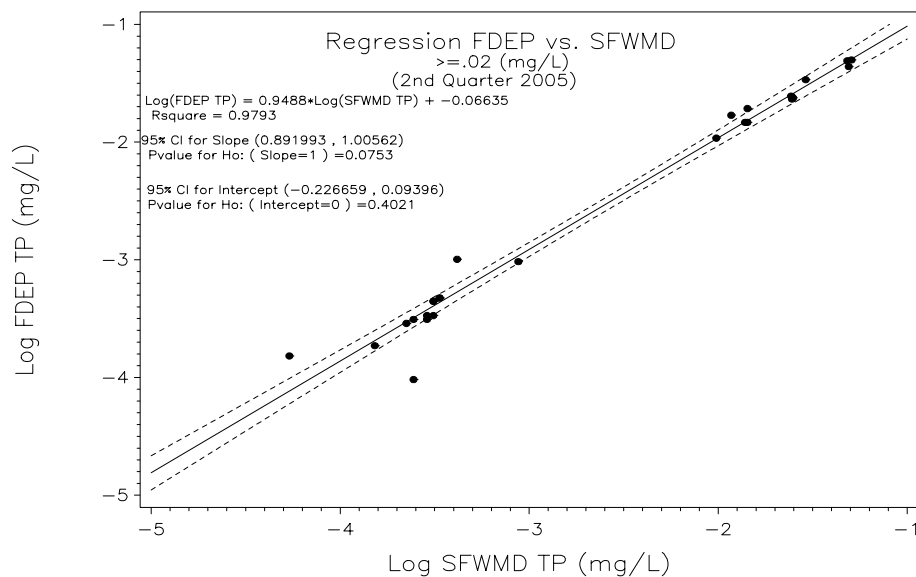


Figure 8. Regression analysis of TP (>0.02 mg/L) recoveries from SFWMD vs. DEP laboratory

B. National Proficiency Testing Results

As a requirement for laboratory certification, the District's laboratory performs proficiency testing (PT) on environmental samples on a semi-annual basis. This study is administered by vendors that have been approved by the National Institute of Science and Technology as PT providers for National Environmental Laboratory Accreditation Conference.

The result of April 2005 study is presented in Table 6.

Table 6. Laboratory Proficiency Testing Results for TP, April 2005

Sample I.D	Reported Value, mg/L	Assigned Value, mg/L	%Recovery	Status	Z-Score
Sample 1 (WP)	3.11	3.15	98.7	Acceptable	0.273
Sample 2 (APG)	0.408	0.413	98.8	Acceptable	0.448

WP=water pollution; APG=Analytical Products Group, Inc.

Glossary

Accuracy. The agreement between the actual obtained result and the expected result. QC check samples having known or “true” value are used to test for the accuracy of a measurement system.

Equipment blank (EB). A general terminology used for analyte-free water that is processed on-site through all sampling equipment used in routine sample processing. May be an assessment of effectiveness of laboratory decontamination (LCEB) or on-site (field) decontamination (FCEB). EB values are indicative of the effectiveness of the decontamination process.

Field Cleaned Equipment Blank (FCEB). Analyte-free water that is processed on-site, after the first sampling site, through all sampling equipment used in routine sample processing. EB values are indicative of the effectiveness of the decontamination process.

Field blank (FB). Analyte-free water that is poured directly into the sample container on site during routine collection, preserved and kept open until sample collection is completed for the routine sample at that site. FB values are indicative of environmental contamination on site.

Laboratory Method Blank. Analyte-free water that is subjected to the entire analytical process. This is not a field-collected blank.

Method Detection Limit (MDL). The smallest concentration of an analyte of interest that can be measured and reported with 99 percent confidence that the concentration is greater than zero. The MDL's are determined from the analysis of a sample in a given matrix, using accepted sampling and analytical preparation procedures, containing the analyte at a specified level. The MDL is determined by the protocol defined in section 40 CFR Part 136, Appendix B as established by the EPA.

Practical Quantitation Limit (PQL). The smallest concentration of an analyte of interest that can be quantitatively reported with a specific degree of confidence. Generally, the PQL is 12 times the standard deviation that is derived from the procedure used to determine the MDL, or can be assumed to be 4 times the MDL.

Precision. The agreement or closeness between two or more results and is an indication that the measurement system is operating consistently and is a quantifiable indication of variations introduced by the analytical systems over a given time and field sampling period.

Relative Standard Deviation (RSD). A measurement of precision, used when comparing more than two results. It is calculated as: $\%RSD = [\text{Std. Deviation}/\text{Mean}] \times 100$

Relative Percent Difference (RPD). A measure of precision, used when comparing two values. It is calculated as: $\%RPD = [\text{Value1} - \text{Value2}] / \text{Mean} \times 100$.

Replicate sample (RS). A second sample collected from the same source as the routine sample, using the same sampling equipment. RS data are compared to routine sample to evaluate sampling precision.

Split sample (SS). A second sample collected from the same sample obtained from the same sampling device. Results for SS are compared with routine sample results; agreement between these two results is mostly an indication of laboratory precision.

Total phosphorus (TP). Form of phosphorus determined analytically using unfiltered samples. Samples are digested using acid reagent, then analyzed colorimetrically.

Total dissolved phosphorus (TDP). Form of phosphorus determined analytically using samples that have been filtered using 0.45 membrane filter. Samples are digested using acid reagent, then analyzed colorimetrically.

Total suspended sediments (TSS). Solids in water that can be trapped by a filter. Analytically, the standard method is to filter the sample using a glass fiber filter and the amount of solids is determined gravimetrically.

Appendix Table 1. TP, TDP, and TSS data in relation to collector, visual observations of particulates, water depth, and whether sampled from helicopter float or accessed by wading, February to June 2005

Station	Date	Total P, mg/L	Total Dissolved P, mg/L	TSS mg/L	Observations on Amount of Particulates in the sample [†]	Total depth, m	Depth to Consolidated Sediment, m	Sampled fr H. Float? ^{††}
Lox3	5/2/2005	NS	NS	NS	NS	<0.1	NO	
Lox4	5/2/2005	0.043	NS	NS	heavy	0.13	0.16	
Lox5	5/2/2005	NS	NS	NS	NS	<0.1	NO	
Lox6	5/3/2005	0.049	NS	NS	light	0.18	0.21	Y
Lox7	5/2/2005	0.108	0.028	148	heavy	0.19	0.22	
Lox8	5/2/2005	0.046	<i>0.007</i>	23	heavy	0.36	0.38	
Lox9	5/2/2005	NS	NS	NS	NA	0.09	NO	
Lox10	5/2/2005	NS	NS	NS	NA	0.05	NO	
Lox11	5/3/2005	0.069	0.007	204	heavy	0.27	0.31	
Lox12	5/3/2005	0.009	0.005	<3	NO	0.61	0.62	
Lox13	5/3/2005	0.015	0.007	11	light	0.32	0.39	Y
Lox14	5/3/2005	0.018	0.004	19	heavy settled	0.37	0.43	
Lox15	5/3/2005	0.009	0.005	<3	low	0.61	0.66	Y
Lox16	5/3/2005	0.012	0.006	<3	light	0.63	0.66	Y
FCEB	5/3/2005	<0.002	<i>0.004</i>	<3	NA	NA	NA	NA
Lox3	6/13/2005	0.023	NS	NS	medium floc	0.17	0.21	
Lox4	6/13/2005	0.016	0.011	<3	medium floc	0.32	0.36	
Lox5	6/13/2005	0.026	NS	NS	medium floc	0.18	0.21	
Lox6	6/14/2005	0.014	0.006	9	medium floc	0.32	0.36	
Lox7	6/13/2005	0.022	0.009	19	heavy floc	0.36	0.37	
Lox8	6/13/2005	0.018	0.008	12	medium floc	0.32	0.34	
Lox9	6/13/2005	0.027	0.009	25	medium floc	0.22	0.27	
Lox10	6/13/2005	0.027	0.006	6	medium floc	0.24	0.26	
Lox11	6/14/2005	0.037	0.007	51	heavy floc	0.41	0.43	
Lox12	6/13/2005	0.007	0.005	<3	no floc	0.77	0.8	Y
Lox13	6/14/2005	0.009	0.004	11	medium floc	0.41	0.45	
Lox14	6/14/2005	0.014	0.005	8	medium floc	0.51	0.54	
Lox15	6/13/2005	0.007	0.005	<3	light floc	0.66	0.72	Y
Lox16	6/14/2005	0.038	0.011	6	very heavy floc	0.53	0.63	
FCEB	6/13/2005	<0.002	<0.002	<3	NA	NA	NA	NA

[†] Based on what was noted on the field notes; according to what was observed in the bucket or bottles during sample processing.

^{††} Based on what was noted on the field notes.

NS=no sample, no analysis; NO=not observed; NA=not applicable